

## PROCESS FOR PRODUCING A CATALYTIC CONVERTER

## BACKGROUND OF THE INVENTION

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[0001] The present invention relates to a process for producing a catalytic converter.

10 [0002] Japanese patent publication JP A 08 134 682 describes an electroplating process for coating a metallic substrate with a smooth precious metal layer, in which an iron-containing substrate is provided with a platinum covering. German patent DE 197 32 170 C2  
15 discloses a process for covering a ceramic SiC substrate in a locally selective manner with a platinum covering, the surface of which matches the rough ceramic surface, as a result of a direct voltage being applied between the substrate and a counterelectrode. The coated substrate is then treated at elevated  
20 temperature of over 400°C.

[0003] European publication EP-A-106 197 discloses a process which forms a starting point for the invention and provides for electrochemical deposition of a porous  
25 platinum layer. The layer is deposited on a carbon or semiconductor substrate. In this process, a one-off high voltage pulse is applied between a substrate and a counterelectrode so that nuclei are deposited on the substrate. There then follows a prolonged pulse at a lower  
30 voltage, during which growth of the nuclei takes place. U.S. Patent 4,273,624 discloses an electroplating process in which a thin, continuous layer of platinum is deposited on an SnO<sub>2</sub> substrate. Japanese patent publication JP A 7 80327 discloses a catalytic converter in which a metallic  
35 substrate is coated with a thin, non-porous layer of precious metal. A lack of pores distinguishes the catalytic converter by a high resistance to oxygen.

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## SUMMARY OF THE INVENTION

[0004] One object of the present invention is to provide a process for coating a metallic substrate which allows deposition of a precious metal with a large surface area and good adhesion to a substrate.

[0005] According to the invention, a layer of catalytically active metallic material is deposited on a metal substrate by way of electrochemical deposition. The substrate is immersed in an electrolyte which contains the catalytically active metallic material, and voltage is applied between the substrate and a counterelectrode. An electric direct voltage on which an alternating voltage is superimposed is applied between the substrate and the counterelectrode, and the catalytically active material is deposited on the substrate as a porous or non-cohesive layer.

[0006] It is particularly advantageous for the substrate to be provided, on its surface which is to be coated, with a predetermined surface roughness prior to the deposition. The surface roughness preferably lies in the range from 0.3  $\mu\text{m}$  to 10  $\mu\text{m}$ . A more preferable range for the surface roughness is between 0.3  $\mu\text{m}$  and 3  $\mu\text{m}$ . The surface roughness is expediently generated by thermal and/or mechanical and/or chemical treatment.

[0007] The catalytically active material is preferably formed from metal clusters with diameters between 2 nm and 1  $\mu\text{m}$ , and preferably between 2 nm and 300 nm.

[0008] One particular advantage of the process is that it is possible to deposit catalytically active layers with a very large surface area and a relatively low level of catalytically active material. The layers exhibit good adhesion and are stable at high temperatures even after prolonged use.

[0009] Preferred catalytically active materials are precious metals. One suitable catalytically active material is platinum. A preferred counterelectrode is formed by platinum-coated titanium sheet. A further  
5 preferred counterelectrode consists of platinum-coated nickel.

[0010] In a particularly preferred refinement of the invention, platinum is deposited with different  
10 morphologies. This provides catalytic converters which have different selectivities for conversion of matter. For example, it is possible to produce a preferred platinum catalytic converter for a reforming reactor which, despite a high carbon monoxide concentration in  
15 an H<sub>2</sub>/CO mixture, has a continuously high activity for hydrogen conversion in operation.

[0011] Further advantages and configurations of the invention will be apparent from the claims and the  
20 description. The invention is described in more detail below with reference to drawing figures.

#### BRIEF DESCRIPTION OF THE DRAWINGS

25 [0012] Figure 1 is a schematic view of a structure for carrying out the process according to the invention,

[0013] Figure 2 diagrammatically depicts a section  
30 through a coated surface,

[0014] Figures 3a-3c show scanning-electron microscope images of the surface of a catalytic converter with dendritic platinum clusters,

35 [0015] Figure 4 shows a scanning-electron microscope image of the surface of a catalytic converter with spherical platinum clusters,

[0016] Figures 5a and 5b show two scanning-electron

microscope images of the surface of a catalytic converter with dendritic platinum clusters before (Figure 5a) and after (Figure 5b) a long-term test,

5 [0017] Figures 6a and 6b show a comparison of rough (Figure 6a) and smooth (Figure 6b) surface profiles of steel substrates prior to the coating with catalyst material,

10 [0018] Figure 7 shows a measurement curve indicating the hydrogen conversion achieved by a catalytic converter with spherical platinum clusters in a CO-containing atmosphere, and

15 [0019] Figure 8 shows a measurement curve illustrating the conversion of hydrogen achieved by a catalytic converter with dendritic platinum clusters in a CO-containing atmosphere.

## 20 DETAILED DESCRIPTION OF THE INVENTION

[0020] Figure 1 shows an arrangement for carrying out the process according to the invention. A function generator 1 generates a modulated voltage which is  
25 amplified in an amplifier 2 and is applied between an anode 3 and a substrate 4 which is to be coated in a deposition bath 5. A direct voltage  $V_{dc}$  is preferably superimposed with an alternating voltage  $V_{ac}$ . The sum  
30 voltage of direct voltage  $V_{dc}$  and alternating voltage  $V_{ac}$  is also referred to below as the modulated voltage  $V_m$ . The alternating voltage is expediently sinusoidal, but may also adopt other forms, for example sawtooth or square-wave form.

35 [0021] The catalytically active material 6 is deposited on the substrate 4 in the form of clusters. According to the invention, the clusters may have different forms which can be predetermined by the deposition parameters. The substrate 4 which is coated

with catalytically active material 6 then forms the catalytic converter.

5 [0022] The direct voltage  $V_{dc}$  is preferably at least as great as the deposition potential of the catalytically active material 6 on the substrate 4, particularly preferably at most 50% higher. The precise level of the direct voltage  $V_{dc}$  is dependent on the constituents and process conditions employed and may, for example, adopt  
10 different values for differently pretreated substrates, although these values do not usually differ greatly from one another. When depositing mixed systems as catalytically active material, it is also possible for the preferred direct voltage  $V_{dc}$  to lie below this  
15 deposition potential.

✓ [0023] Stainless steel, particularly Cr-Ni steel 1.4541, CR-Ni steel 1.4571 or Cr-Al steel 1.4767, is used as a particularly suitable substrate. It is  
20 expedient for the substrate to be sand-blasted or roughened in some other way, for example chemically, and to undergo alkaline degreasing prior to the coating. This improves the adhesion of the catalytically active material 6 to the substrate 4.

25 [0024] In a preferred embodiment, the alternating voltage  $V_{ac}$  has a maximum voltage swing  $V_{pp}$  between minimum and maximum which is lower than the direct voltage  $V_{dc}$ , so that overall the sign of the sum voltage  
30 between substrate 4 and counterelectrode 3 does not change.

[0025] The current between substrate 4, which serves as the cathode during the deposition, and anode 3 is  
35 recorded and, in accordance with Faraday's law, is used as a measure for determining the quantity of catalytically active material 6 deposited, this material being contained in the deposition bath; current contributions which flow for the purpose of

building up and breaking down the electrolytic double layer on account of the modulation are expediently eliminated, since they do not originate from the reduction or oxidation of cations or anions.

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[0026] It is preferable to deposit precious metals in order to produce the catalytic converter. However, it is also possible to deposit mixtures of precious metals. An expedient, inexpensive anode is platinum-coated titanium instead of a standard sacrificial anode made from solid platinum, which can be used to particularly good effect if platinum is to be deposited as catalytically active material. However, other precious metals and also other metals can be deposited in this inventive way.

[0027] The frequency and/or the amplitude  $V_{pp}$  and/or the voltage offset  $V_{dc}$  of the modulated voltage can be adjusted in order to optimize the deposition parameters for the particular system. The values affect both the size of the clusters which are deposited on the metallic cathode and their morphology. Overall, the clusters on the substrate 4 constitute a large active surface area for catalytic reactions. The optimum cluster size can be set in each case for different applications by suitably selecting the deposition parameters and the duration of coating.

[0028] It is particularly advantageous for the surface of the substrate 4 which is to be coated to be roughened prior to the coating, for example by pickling or sand-blasting. Other methods for increasing the surface roughness are also possible. This is illustrated in Figure 2 with reference to a diagrammatic side view of a coated surface. A substrate 4 has a roughened surface 4.1 on which spherical metal clusters 6.1 are arranged in recesses. The metal clusters 6.1 may also be deposited on the peaks or the flanks of the roughened areas.

[0029] The increased surface roughness has the advantage that deposited clusters 6.1 adhere more successfully to the substrate surface, and undesirable combining of the clusters 6.1 is suppressed. A catalytically active layer of individual clusters 6.1 is formed; the layer is preferably not continuous, but rather is formed from isolated clusters 6.1.

10 [0030] The surface roughness is preferably between 0.3  $\mu\text{m}$  and 10  $\mu\text{m}$ , particularly preferably between 0.3  $\mu\text{m}$  and 3  $\mu\text{m}$ . A large active surface area is formed from the finely distributed clusters 6.1. A further advantage is that the increased surface roughness also  
15 contributes to increasing the surface area of the substrate 4 and therefore also the chemically active surface area. At the same time, the clusters 6.1 can be very small, so that overall only a small quantity of the expensive catalytically active material 6 has to be  
20 deposited, yet at the same time the catalytic converter is distinguished by a high catalytic activity.

[0031] The adhesion of the metallic clusters 6.1 to the substrate surface 4.1 is very good. This makes the  
25 catalyst layer more resistant to erosion.

[0032] A particular advantage over conventional catalyst layers is that, according to the invention, good heat transfer from the catalyst layer to the  
30 substrate 4 is possible, since metallic clusters 6.1 are joined to a metallic substrate 4. By contrast, known, conventional catalyst layers are produced, for example, with supported catalyst materials, in which ceramic support particles are coated with a precious  
35 metal. In this case, the heat transfer between catalytically active precious metal and a substrate is significantly worse, since the ceramic particles arranged between them have only a low thermal conductivity. In addition, in a catalytic converter

which is produced according to the invention, it is also possible to dispense with standard adhesion promoter layers, which have an additional adverse effect on the heat transfer properties between catalytically active material 6, 6.1 and substrate 4.

[0033] A substrate 4 which is coated according to the invention is therefore particularly suitable for use as an oxidation catalytic converter for treating exhaust gases in fuel cell systems. A further expedient application is for various heterogeneously catalysed processes. The catalytic converter according to the invention and the process according to the invention are particularly advantageous in exhaust-gas catalytic converters for vehicles.

[0034] Figure 3 shows scanning-electron microscope images of preferred catalytic converters with dendritic platinum clusters (Figures 3a, 3b), and with rhodium clusters which are of substantially dendritic form.

[0035] Dendritic platinum clusters are preferably deposited on a stainless steel substrate as a result of a direct voltage  $V_{dc}$  of 1.4 volts being superimposed with an alternating voltage  $V_{ac}$  with  $V_{pp}=0.75$  volt (peak-peak voltage swing) and the modulated voltage being applied between a stainless steel substrate and a counterelectrode. The frequency of the alternating voltage  $V_{ac}$  is 10 Hz. The electrolyte used is platinic acid, in particular hexachloroplatinic acid, with a platinum content of 0.1 g/l. The deposition preferably takes place at room temperature.

[0036] The platinum clusters present dendritic growth, and no spherical platinum clusters are observed. The preferred catalytic converter has a high level of activity for hydrogen conversion even in the presence of carbon monoxide, carbon monoxide also being converted with a good yield at the same time.



[0037] In the selected system, dendritic platinum clusters are deposited with frequencies of between 5 and 15 Hz and an alternating voltage  $V_{ac}$  with a voltage swing  $V_{pp}$  of between 0.3-1 volt.

[0038] A further preferred catalytic converter is produced by deposition of rhodium on stainless steel, preferably comprising stainless-steel sheet 1.4541, 1.4571 or 1.4767. It is also possible for mixed catalysts of platinum to be deposited in this way or to deposit catalysts comprising mixtures of precious metals and/or catalytically active materials, such as for example PtRh, PtRu, PdPt.

[0039] Deposition takes place from a solution of 0.2 g/l of rhodium in 0.1 M  $H_2SO_4$  at room temperature with a direct voltage  $V_{dc}$  of 1.4-1.6 volts and a superimposed alternating voltage  $V_{ac}$  with  $V_{pp}=1$  volt (peak-peak amplitude) and a frequency of 10 Hz. The formation of dendritic growth of the clusters can be improved still further by varying the voltage parameters.

[0040] A catalytic converter of this type has a good activity for methanol. A catalytic converter of this type is therefore particularly suitable for use in fuel cell vehicles operated with methanol, particularly preferably in catalytic burners.

[0041] Figure 4 shows a scanning-electron microscope image of a further preferred catalytic converter with spherical platinum clusters. The deposition takes place using a direct voltage  $V_{dc}$  of 1.2-1.4 volts and an alternating voltage  $V_{ac}$  with  $V_{pp}=0.4$  volt and 100 Hz; the deposition bath otherwise corresponds to that used for Figure 3.

[0042] In this system, an alternating voltage  $V_{ac}$  with frequencies of more than 50 Hz, preferably up to

150 Hz, is preferably used for the deposition of spherical platinum clusters. The direct voltage  $V_{dc}$  which is applied varies with the substrate pretreatment and, for the deposition of spherical clusters, is substantially equal to or tends to be slightly lower than that used for the deposition of dendritic clusters.

✓ 10 [0043] Figure 5 shows a comparison of scanning-electron microscope images of a catalytic converter with dendritic platinum clusters before (Figure 5a) and after (Figure 5b) a long-term test, in which the catalytic converter was exposed to an  $H_2/CO$  mixture at high temperature for more than 200 h. Although exposed 15 to high temperatures of up to  $600^\circ C$ , the porous or non-cohesive platinum layer as catalyst remains stable; the clusters remain fixed in position and do not converge. The layer which has been deposited in accordance with the invention demonstrates that the clusters in 20 practice do not change before and after long-term use.

✓ 25 [0044] Figure 6 shows a comparison of rough (Figure 6a) and smooth (Figure 6b) surface profiles of steel substrates which have been used for the deposition of the platinum. The adhesion of the platinum clusters to the roughened substrate is significantly better than the adhesion to the smooth substrate; the layers are wipe-resistant, while the layers on an untreated, smooth substrate are not wipe-resistant. The surface 30 roughness is preferably between  $0.3\ \mu m$  and  $10\ \mu m$ , particularly preferably between  $0.3\ \mu m$  and  $3\ \mu m$ .

35 [0045] The catalytic activity and/or selectivity of the catalytic converter differs depending on the particular form of the clusters. A preferred catalytic converter with spherical platinum clusters converts hydrogen in a substantially selective manner. The catalytic converter is poisoned and has a greatly reduced activity in the presence of carbon monoxide. A

catalytic converter of this type is preferably used under carbon monoxide-free conditions.

[0046] By contrast, a preferred catalytic converter with dendritic platinum clusters firstly has a high tolerance to carbon monoxide during the hydrogen conversion and secondly has a high selectivity and high activity both for the hydrogen conversion and for the carbon monoxide conversion.

[0047] Figure 7 shows a measurement curve illustrating the hydrogen conversion achieved by a preferred catalytic converter with spherical platinum clusters. The catalytic converter is exposed to an  $H_2/CO$  mixture under standard operating conditions. After even a few minutes, the hydrogen conversion in the presence of CO falls to low levels.

[0048] Figure 8 shows a measurement curve illustrating the hydrogen conversion achieved by a preferred catalytic converter with dendritic platinum clusters. In this case too, the catalytic converter is exposed to an  $H_2/CO$  mixture under standard operating conditions. However, the measurement curve shows that the conversion of hydrogen and for carbon monoxide remains at substantially constant high levels over more than 200 hours. The conversion can in each case be improved further, since the operating conditions have not been optimized.

[0049] A catalytic converter which has been produced in accordance with the invention is particularly resistant to erosion, and its production can be successfully reproduced. The deposition parameters of the catalytically active material on the substrate can easily be optimized for different materials which are to be deposited by suitably selecting the direct voltage  $V_{dc}$ , alternating voltage amplitude  $V_{pp}$  and/or frequency. Process control is simple, and the catalytic

converter properties can be reproducibly set by simple modifications to the deposition process. The yield of material is good, so that, for example for highly active platinum catalytic converters, relatively small quantities of the precious metal have to be used.

[0050] A preferred use for a catalytic converter produced according to the invention is use in a CO-rich environment, in particular in an exhaust-gas cleaning system in a motor vehicle. A further preferred use of a catalytic converter according to the invention is its use in a fuel cell system.